R. T. Vanderbilt

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REVIEW OF CURRENT TECHNIQUES FOR THE ANALYSIS OF FIBERS IN TALC

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I. INTRODUCTION

A. Talc as a biologically active substance

Occupational exposure to tale dust in the work place has been associated with the development of lung scarring which has been termed talcosis.1-3,12,13,15 Clinicians have described talcosis as a fine, diffuse, bilateral progressive scarring which may, if severe, produce disability or premature death. In addition to scarred lungs, reports have suggested that excess malignant tumors occur among these workmen.14 Some investigators have suggested that "fibrous tales" possess greater fibrogenicity than the platy varieties.5,11 This observation, as well as evidence suggesting that talc-associated diseases resemble asbestos diseases,3-5 has prompted investigators to suggest that the fibers within the talc are the biologically active agents. Yet, a number of clinical observations have demonstrated that nonfibrous platy talc may produce disease in occupationally exposed workmen.6-10

Some talc rocks are naturally contaminated with the asbestiform amphibole minerals anthophyllite and tremolite. Both tremolite and anthophyllite exposures have been shown to be associated with excess disease in workmen exposed to these minerals as aerosols. 16-23 Some investigators suggest that any fiber reaching the terminal bronchioles and alveolar spaces may induce pathogenic responses, 24-27 which raises the question whether "pure" talc fiber, with fibrous rather than platy crystal habit, may be biologically active. These interesting observations have prompted the study of the natural mineral contaminants in currently marketed consumer talcums and powders. No evaluation can be made concerning the possible biological hazards associated with talc use, either

in an industrial or consumer product setting, unless the nature of the materials themselves are known. One objective of this study was the development of the analytical techniques required to answer this fundamental question.

B. Talc as a mineral

Talc has been defined as a mineral species on the basis of its structure, chemistry and physical properties.28-32 Its geological origin is complex. The initial rock-types, metamorphic processes and minerals are so diverse that the talc end-product is often a complex mixture of many magnesium silicate minerals. Laboratory studies of talc mineral synthesis,33-31 and mineralogical studies of the materials themselves 15,35,36 have demonstrated the intimate association, and, in some instances, intergrowth of talc mineral with other minerals (e.g., tremolite and anthophyllite). Such mineralogical curiosities, now being discovered with increasing frequency, include the "talcboles," which are mineral species consisting of mixed structures intermediate between amphibole double chains and talc infinite sheets.37 Talc rock, as mined, may therefore contain platy talc minerals, tale fibers, asbestiform anthophyllite, tremolite, hexagonite and tirodite, and the fibrous serpentine mineral chrysotile. Numerous other minerals, such as chlorite minerals, the carbonate minerals, pyrophyllite, feldspar, micas and quartz also occur naturally with talc. These have been described in detail elsewhere.38-43

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C. Talc as used in society

In the United States there are presently several grades of tale commonly in use. These grades are based upon the relative purity of the product, the physical and chemical properties of the material, and its ultimate use. One important grade is pharmaceutical tale, which is used for cosmetic purposes. It is reported to contain at least 90% platy tale mineral, and no detectable asbestos.41 Several studies have shown, however, that highly contaminated products have found their way to the market place. 38,39,45 The analysis of pharmaceutical grade tale, and cosmetic talcum products, has been the subject of a recent report.35 The analytical procedures required for the detection of low-levels of asbestiform minerals in consumer tales form the basis of the present communication.

II. INSTRUMENTAL TECHNIQUES FOR FIBER ANALYSIS

A number of instruments have been used for the analysis of mineral fibers in talc products, each with its uses and limitations. These techniques include optical microscopy, x-ray diffractometry, and electron beam instrumentation.

A. Optical microscopy

Optical microscopy is a widely used instrumental technique for the mineralogical analysis of talc and talcum products. Dispersion staining enables the investigator to determine the indices of refraction of the object in view. 46.47 Dispersion staining—using bright field microscopy, with an annular stop—is a standard technique for the identification of minerals. With the use of immersion oils of known refractive indices, and the measurement of the optical properties of the crystalline object studied, mineral identity and chemistry may be determined with great accuracy.

However, there are many limitations to optical microscopic methods. 38,48,49 The accurate determination of refractive indices is extremely difficult for particles less than 1 μm in width; the optical properties of fibrous minerals commonly found in tale frequently overlap, allowing only tentative identification; orientations of the particles are often random so that only a range of the refractive indices may be measured; optical characteristics such as birefringence may vary greatly from the "standard values" because of small particle size; similar mineral phases may be present in the same specimen producing overlapping properties.

Although light microscopy has severe limitations for the analysis of pulverized rock specimens (talc) it is often suited for the preliminary scan of materials in determining the overall degree of contamination. Mineral phases, present in quantities so small as to

escape detection by x-ray diffractometry, may often be observed by optical microscopic methods. It is well to remember that the light microscope must be used only as a preliminary analytical tool since asbestiform mineral fibers, occurring as contaminants in a larger mineral habit, often lie below the resolution of the light microscope. 19

B. X-ray diffractometry

X-ray diffractometry is one of the standard mineralogical techniques used in the analysis of crystalline substances. Crystalline materials may be subjected to x-ray bombardment and caused to "reflect" from their atomic planes a characteristic x-ray spectrum. This has been termed a structural "finger-print" and may be used to identify, in most instances, which crystalline phases are present in the sample. The width of the reflections, and their relative intensities, may reflect absolute particle sizes of the phases. In addition to the identity of the mineral phase, shifts in interatomic periodicities may reflect chemical variations.

Powder x-ray diffractometry has been used in both the continuous scan and step-scan modes of operation for the identification of asbestiform mineral phases in talc and talcum products.48 These x-ray techniques have also been used to quantitatively determine the asbestiform mineral content of consumer spackling and plastering compounds.⁶⁵ The proper use of this instrument entails the following requirements: 48,50 1) the selection of a number of standard minerals of high purity to be used for comparison purposes in the development of calibration standards for quantitative x-ray diffractometry, (i.e., a tale mineral of high purity to be used as a "matrix" and mineral fibers which are not contaminated with other mineral phases): 2) the preparation of talcasbestiform fiber mixtures for the development of dilution standards for quantitative x-ray diffractometry; 3) the use of a sample preparation technique which is sensitive and reproducible; 4) the selection of non-interfering x-ray reflections specific for an individual mineral species.

In addition to the sample preparation and instrumental factors which affect the reproducibility of the system, a number of other factors affect the lower limits of detection of specific mineral phases dispersed in a talc matrix. These include: instrument geometry, design of x-ray diffraction equipment and proper scan speed. chemical makeup of the various components, particle size of components, preferred orientation of components, sample thickness, sample flatness and mass absorption characteristics of the material. There are also a number of "special factors" which also influence the reproducibility and relative accuracy of these determinations. 50,52,53,54

The limits of detection of asbestiform minerals in a talc matrix have been determined 35 as follows:

chrysotile, 0.25 to 0.5%; tremolite, 0.1%; anthophyllite, 2.0%. These detection limits are based upon the establishment of standard dilution curves which were determined from binary systems, although in most talc mixtures there are often two or more mineral phases. The sorption characteristics of major components are such that the comparison of unknown mixtures with the standard dilution curves yield conservative estimates of asbestiform mineral concentration.

Recently, the question has been asked: are fibrous amphiboles in talc equivalent to their asbestos analogs? For example, asbestos and asbestiform (non-asbestos) varieties possess different optical properties based on fiber structure (contiguous vs. parallel intergrowth of subunits) and their different cleavages. Both asbestos and asbestiform (non-asbestos) mineral analogues possess cleavage parallel to (010). Whereas rock-forming amphiboles possess prominent (110) cleavage, the asbestos analogues apparently do not. One can readily appreciate the importance of a preparation technique which eliminates such orientation effects.

The major drawback of x-ray diffractometry as an analytical tool in determining the fiber contents of tales and talcums is the inability to distinguish shape (i.e., asbestiform particles from fragmented fibers or equidimensional particles). To do this requires the use of other instrumentation, particularly light or electron microscopy.

C. Transmission electron microscopy (TEM)

Since the size distribution of fibers in talcs and talcum products is often smaller than the resolution limit of light optical microscopy, large numbers of fibers may not be detected by this technique. TEM affords the opportunity to examine all particles visually and permit identification and characterization in most instances.

Tale may be prepared for TEM examination by sonically dispersing in distilled and filtered water, and directly pipetting onto Formvar-carbon-coated 200 mesh nickel locator TEM grids. After drying, the grids may again be carbon-coated to ensure a thermally and electrically stable preparation. Sonically dispersed aliquots may also be directly filtered through membrane or polycarbonate filters and directly transferred onto TEM grids through chemical dissolution techniques. Again, a film of a conductive material is required to ensure stability under the electron beam. (These techniques are described in many papers at this conference.) An alternative technique disperses particles in a drop of nitrocellulose solution on a glass slide. A second glass slide is placed on the first and the two are drawn apart, lightly, leaving a film. Films are then directly transferred to TEM grids. This technique is intended

to minimize the alteration of particle size distribution.

Samples thus prepared should be examined by TEM using accelerating voltages in excess of 100KV to ensure particle penetration. Scan magnifications may vary from 1500X to 40,000X direct.^{48,55}

The visualization of diffraction contrast images on the TEM screen, and their photographic recording, is necessary. Morphological characteristics, including length to width ratios, diffraction contrast figures, cleavage characteristics, edge characteristics and beam damage sequelae may be used in the characterization and identification of fibers in talc. 55,56 Although amphibole fibers in talc may possess various morphologies, chrysotile fibers may be identified on a morphological basis alone. 45,55,60,62

While amphibole fibers may be distinguished from chrysotile on a morphological basis, very often it is difficult to distinguish tale fiber from amphibole fiber in the same specimen. Occasionally, tale fibers possess prismatic truncations which help distinguish between these mineral types. The morphological data determine length to width ratios and the size distribution of the fibers present. Often, structural characterization is required to distinguish between these mineral types.

D. Selected area electron diffraction (SAED)

Utilizing TEM, the diffraction image in the back focal plane of the objective lens may be focused on the viewing screen by means of defocusing the intermediate lens. In this manner, the image of the scattered electrons, related to diffraction effects consistent with the Bragg geometry, may be observed on the TEM screen.

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Crystalline materials tend to scatter electrons in regular patterns which are related to the arrangement of atoms and the interplanar spacings between the atoms. This geometry is similar to that of the Laue method (fixed crystal and film) which enables the microscopist to determine interplanar spacing dimensions and planar angular relationships. 55,57,58,80,82 A number of papers have been published which also deal with this technique (e.g., see Lee, this conference 58). SAED patterns have been described for chrysotile, 55,60,62 for the amphibole asbestos minerals, 48,61 and for fibrous minerals in talc. 38

For most accurate results, gold can be evaporated onto the same surface for use in calculation of the camera constant of the instrument. Because of the small particle size of evaporated gold, its selected area electron diffraction pattern consists of Debye-Scherrer rings. Gold, having known interplanar spacings, may be used to accurately determine the camera constant of the instrument under those specific conditions of operation. After obtaining a SAED pattern on a single fiber of interest (with

superimposed gold "rings"), the analyst may accurately determine the fiber interplanar spacings. Routinely, the pattern is photographed on film, cut to an appropriate size to fit a Philips film reader, and reflection periodicities measured to within \pm 0.01mm. Preliminary evaluation of the pattern permits determination of the Laue zone.

Generally, the two reflections nearest the center (000) are measured and their distances and angular characteristics determined. These reflections are assigned an index, and the calculated spacings and angular characteristics compared with known values for the mineral species. This technique has recently been automated.

The published patterns for amphiboles are varied, reflecting not only different mineral species, but a number of variables which are both specimen and instrumental in nature. One of the major shortcomings in obtaining a characteristic SAED pattern from an amphibole is the orientation effect. Asbestiform amphiboles (rock-forming silicates) normally cleave with a (110) or (210) orientation. Asbestos fibers, on the other hand, do not cleave well in these directions but rather in the (010) plane.51 In effect amphibole asbestos patterns are produced with be planar projections, displaying b* and c* axes and periodicities. Occasionally, one sees the same projection for the asbestiform amphiboles, but this is not as common. Frequently the use of a goniometer stage is required for reorienting these crystals along a principal zone axis so that one of the principal Laue zone axes is obtained. Thin fibers often do not yield enough constructive interference for the production of SAED patterns; thick fibers do not permit penetration of the beam, and therefore do not produce patterns at all. Intermediate between these dimensions (which are related to a number of factors including accelerating voltage of the instrument) a range of diffraction effects may occur, from a twodimensional array to a more complex three-dimensional array. This has yet to be studied.* Yet, despite these difficulties, one may distinguish amphibole fibers from talc fibers. In the future, with careful work, perhaps amphibole species may be distinguished with this technique.58

E. Electron microprobe analysis of single crystals

The electron microprobe technique is based upon the concept that high energy electron bombardment of solid inorganic specimens causes the generation of x-rays characteristic of the elements present in that particular specimen. There are two major probe techniques used for microchemical analysis today: wavelength dispersive focusing crystals, and energy dispersive x-ray analysis. A comparison of both techniques has recently been made.

The analysis of single fibers has been achieved utilizing both of these probe techniques. 48,64 There are a number of sample and instrumental factors, which affect the output of chemical information with the x-ray spectrometry method. Although we have used wavelength dispersive focusing crystals, with excellent resolution, the system is relatively inefficient. The time of elemental scan is increased by the fact that only one element may be analyzed per unit time per crystal, and extremely high beam currents are required for small particle analysis. Although large crystals are easily analyzed with the wavelength dispersive technique, the time of elemental scan is such that it precludes large numbers of fibers from analysis.

Utilizing energy dispersive systems (EDXA) and field emission ("cold cathode") electron sources, virtually any fiber in a talc sample may be analyzed in an extremely short period of time. Although the ability to resolve light elements is not as good as with the wavelength dispersive system, the method is rapid and an entire spectrum may be obtained (atomic No. 11 and higher) in a short time. One of the drawbacks to this method is the requirement that the energy dispersive x-ray spectrum be compared with standards. The chemical information consists of a complex spectrum consisting of the specific line of interest, background radiation, and other superimposed peaks. Methods are now being developed for digital spectrum filtering of the peaks of interest, in which the entire spectrum is parameterized by a square search function. 6.3 Semiquantitative chemical analysis of unknown particles may be obtained in the near future.

Microchemical analysis of amphibole fibers is currently required for unique identification. A number of reports at this conference concur that this technique is indispensable for single fiber analysis.

F. Other techniques

We have found that a bulk chemical analysis, with trace metals of the materials under investigation aids the identification of fibers in talc. For example, knowledge of the total iron content of the sample may yield information as to the amount of anthophyllite in the sample when compared with the alumina, soda, and potash contents (which are also related to the chlorite, mica, and feldspar present). Silica content reflects both sample purity in terms of chlorite content and quartz content of the samples. Lime content may be used to gauge the carbonate and tremolite contents of the sample.

The subject was discussed informally with Dr. Malcolm Ross at the symposium. Scientists using this technique note that some of the different diffraction patterns produced with the 1000 KV TEM, may in part be due to diffraction on thick crystals. The 1000 KV beam is able to penetrate these objects sufficiently to produce diffraction patterns. Workers who use 100 KV machines will essentially be dealing with "thin crystals" and may produce substantially different patterns.

III. ANALYSIS OF FIBERS IN TALC

The following steps are recommended as a suitable technique for fiber analysis of tale:

Optical microscopy should be used as a preliminary scanning tool. Polarized optics should be employed for the determination of the optical properties of all large fibrous objects in the sample. Immersion oils for the determination of indices of refraction should also be employed. Light optical microscopy may permit the identification of mineral phases present, depending on the particle size; it may however permit large numbers of asbestiform minerals to go undetected;

Specimens should be analyzed by x-ray diffractometry. Both continuous and step-scan modes of analysis should be performed on the samples, with step-scanning in diagnostic regions of the spectra for anthophyllite, tremolite, the serpentine

minerals, and quartz;

- 3. Specimens should be analyzed with electron beam instrumentation. TEM is most useful for determining the general morphological characteristics of fibers present, and for the determination of the characteristic structures of these fibers by means of SAED. Routinely, talc fibers may be distinguished from amphibole fibers with this method. Perhaps, with specialized techniques, different amphibole fiber species may be differentiated as well:
- 4. Fibers on electron microscope grids, may also be subjected to electron bombardment for x-ray spectrometry purposes. An electron probe technique utilizing either wavelength or energy dispersive x-ray analysis may be used to acquire the characteristic chemical spectrum. On the basis of morphology, structure, and chemistry, all fibrous objects in talc may be properly identified;

 If facilities permit, the bulk chemistry and trace metal contents of the tale and talcum products

may be determined as well.

The accurate determination of fibers in talcs is possible utilizing a range of instrumental techniques widely available today. The major limitation in such analyses is the time required for such an analysis to be made, the cost of the instruments involved and the expertise required for interpretation. One complex sample, with several different fibers and quartz, may require as much analytical time as one week and cost \$500.00 to properly characterize. This is without bulk or trace chemical analysis.

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Materials

Seven (7) vials containing gram quantities of white powders were among the talc specimens in our laboratory. These vials were labelled: X, 3X, 5X, FT, NYTAL 300, 325, NYTAL 400. These numbers and codes correspond to those talcs studied by Dr. Arthur Rohl, and were the subject of a mineralogical report to NIOSH in 1976. Dr. Rohl directed his report to Mr. John Dement of NIOSH in Cincinnati, Ohio.

We examined these specimens by polarized light microscopy, continuous scan x-ray diffractometry and by analytical electron microscopy. The results of our study are given below.

Light Microscopy

Each of the specimens were studied by polarized light microscopy. Approximately 0.5 mg of powder was removed from each vial and placed on clean glass slides. The powders were immersed in mounting oil with a refractive index of 1.602 ± 0.002 , mixed in the oil with the edge of

another glass slide and then cover-slipped. The specimens were examined by both polarized light microscopy and interference microscopy. 1

We noted the presence of talc, both in plate and fiber form, serpentine minerals (plates only, no chrysotile asbestos noted), tremolite, a carbonate mineral, and traces of quartz. It is crucial to stress the following: all the high aspect ratio fibers (those which are finely fibrous with parallel extinction) display an index of refraction parallel to elongation less than 1.602. Based on the nature and behavior of the Becke line we would conclude that the indices of refraction parallel to the elongation are about 1.590-1.594. These optical properties suggest these fibers are talc. We stress that only one fiber, found in specimen NYTAL 300, had an index which we estimate at the upper limit to be 1.608. This was the single fiber out of the many hundreds examined, and we conclude it was possibly a mixture of talc and an amphibole mineral 2 on a fine scale. We failed to find a single finely fibrous, high aspect ratio fiber which displayed indices characteristic of anthophyllite (minimum n parallel to elongation of > 1.614). The anthophyllite content is therefore less than 1 in about 200 fibers (0.5%).

Although we are presenting the major findings here it is important to note that we also examined the powders in mounting oils with indices ranging from 1.515-1.640. The lower indices of refraction permitted better visualization of talc, serpentine plates and other mineral components of the powder. The higher indices were used to confirm the identification of the tremolite present. We had also scanned the specimens in an oil with $n=1.592\pm0.002$. We observed that many of the high aspect ratio fibers, composed of 1-2 micron fibrils, had indices just above this value (a weak, diffuse, Becke line) which suggested a slightly higher index parallel to the fiber's elongation. Based on the indices of refraction of talc and anthophyllite we re-examined all the talcs in an oil of refractive index equal to 1.602. All of the borderline fibers showed indices consistently below this value. We therefore report and discuss results based on examination of the specimens using this immersion oil.

Based on probe analysis of fiber by AEM we originally suspected anthophyllite as the mixed amphibole phase in talc. However, based on limited x-ray data and lack of structural compatability, another magnesium amphibole mineral may be present

The talc specimens examined ranged in mineral assemblage, i.e., components constituting the assemblage. However, the specimens were almost exclusively talc (both plates and fibers), tremolite³ (cleavage fragments, with short aspect ratios), serpentine plates, a carbonate mineral and a trace of quartz. We failed to find and unequivocally identify pure anthophyllite by the polarized light microscopy technique. Only one fiber out of many hundreds displayed optical properties consistent with a mineral mixture. The high aspect ratio, very fine fibers appear to be talc. Fine, fibrous talc has been described in the mineralogical literature as agalite and has been reported in deposits at Edwards, New York.

X-ray Diffraction Study

Each of the specimens was examined by continuous scan x-ray diffractometry utilizing a Philips 1700 series automated diffractometer. The powders were examined by standard procedure using standard protocol:

Note that we have examined these specimens by interference microscopy as well, utilizing Hoffman optics. The tremolite particles are clearly cleavage fragments. We have failed to find a single high aspect ratio, finely fibrous, tremolite fiber. We conclude that the specimens do not contain tremolite asbestos.

Cu/Ni target/filter at 40 Kv/17 mA, 1° 2 theta/minute, 1000 CPS full scale, TK = 1 second. The results were as follows:

TABLE 1: Characterization of Talcs by X-Ray Diffraction.

Mineral	Tremo	lite	Talc	Serpe	ntine	Carbonate
				(Clinochrysotile)		
Diagnostic Reflection(s)	(110)	(020)	(002)	(002)	(004)	(104)
d-spacing of reflection	8.38Å	8.98A	9.34Å	7.31Å	3.65Å	3.3Å
(intensity of reflection)	100	16	100	100	70	100
Specimen	Intens	sities	<u>Intensity</u>	Ratio I(0	002)/I(004)	Intensity
X 3X 5X FT 300 325 400	100 100 100 72 91 68 72	15 15 8 10 7 7	41 57 60 30 61 49 35	45/29 58/34 28/19 38/26 28/20 30/20	= 1.43 = 1.55 = 1.71 = 1.47 = 1.46 = 1.40 = 1.50 = 1.29	65 45 38 30 61 49 35

Quartz could not be resolved in these mineral mixtures. The quartz (101) reflection, which has an intensity (I) = 100 with a d-spacing value of 3.34\AA , is obscured by the tremolite (141;250) reflection, I = 30, with a d-spacing value of 3.36\AA . The quartz (100) reflection, I = 35, with a value of 4.26\AA was observed on only 1 of 7 tracings as a small signal just recognizable on the baseline. The peak was not statistically significant. The quartz content of these specimens is less than 1% by weight.

The 3.03Å d-spacing does <u>not</u> appear to be the (610) reflection of anthophyllite. The intensity for (610) is 100, and therefore would necessarily be the most intense reflection on a diffraction tracing for this mineral. Other major anthophyllite peaks were obscured by tremolite and talc e.g., the (020), with a value of 8.9\AA (tremolite), and the (410), with a value of 4.50\AA (tremolite) etc.

Careful examination of the peak originally designated as (610), anthophyllite, shows it to occur at a two theta angle of about 29.40° rather than 29.30° . This shifted the d-spacing toward a smaller value. Rather than 3.05Å d-spacing value, a "good" fit for the (610) of anthophyllite, the peak occurs with a value of 3.03Å, a better fit for the (104) reflection of calcite. Several other calcite peaks were observed (2.49Å, 2.29Å and 2.09Å).

This interpretation of the x-ray data fits the optical data better. It is possible that there exists some residual, large, amphibole domains in the fibrous talcs. On the basis of both x-ray and optical studies, discrete amphibole fibers other than tremolite were not detected. As it is detectable by x-ray, it is in concentrations below several tenths of a percent of the specimens; it is submicroscopic in size and may be in the talc as an intergrowth.

Tremolite is present in the specimens examined. Mineral habit could not be distinguished using x-ray techniques. Optical microscopy indicates it occurs as cleavage fragments and is non-asbestiform.

Talc is present in the specimens examined as both fiber and plate. Mineral habit could not be distinguished by x-ray diffractometry.

One of the non-fibrous serpentine polymorphs is also present in the specimens examined. We used a ratio of (002)/(004) as a measure of serpentine content. Some chlorite appears to be present in the mineral specimens; mica has been identified in six of seven specimens.

Analytical Electron Microscopy

Each of the specimens was studied by analytical electron microscopy.

A JEOL 100CX STEM interfaced with a Tracor Northern TN 2000 energy dispersive x-ray spectrometry system was used for this purpose. A

standard laboratory procedure was followed utilizing an accelerating voltage of 80Kv, a beam current of about 100uA and a detector-specimen interface angle of 40°.

In order to characterize the magnesium-silicate population we first studied a number of mineral standards:

TABLE 2: X-ray Ratios of Magnesium Silicates

Mineral Standard	Empirical Formula	Atom Mg:Si Ratio	Weight <u>Ratio</u>	X-Ray <u>Ratio</u>
Talc - Dillon MT	Mg3Si4010(OH)2	3:4	0.64	0.38 ± .08
Anthophyllite ⁴ - Paakila	Mg ₇ Si ₈ 0 ₂₂ (OH) ₂	7:8	0.75	0.41 ± .05 0.50 ± .05 (with Fe)
Serpentine - UICC B - Rockville	Mg ₃ Si ₂ O ₅ (OH) ₄	3:2	1.29	0.80 ± .05

The serpentine polymorphs could be easily distinguished from talc and "anthophyllite" both on the basis of selected area electron diffraction and bulk chemistry. Talc plates yield SAED patterns which are clearly distinguishable from the "anthophyllite." The low Mg:Si ratio further aids as a distinguishing diagnostic for the mineral. However, when the "anthophyllite" does not contain Fe, and when the talc is fibrous, and is positioned at a https://distinguish. are almost impossible to distinguish. This difficulty further

⁴ The chemistry of anthophyllite reported to be present by Rohl (1976), was used as the standard magnesium amphibole.

increases if the minerals are intergrown. As intergrowths exhibit elements of each mineral, their SAED patterns are complex and extremely difficult to interpret. The chemistry is also a mixture of the two minerals impossible to distinguish because of their similar Mg:Si x-ray ratios (Table 2) which cannot be distinguished with this technique. Only two fibers in all the specimens examined were identified as a magnesium amphibole; the remaining fibers were talc and talc amphibole mixtures Based on the light microscopy and x-ray diffraction results we would conclude that the free magnesium amphibole content of the talcs is trace (less than 1%).

Tremolite on the electron microscopic level exists as fragments with an occasional particle with aspect ratio of about 5:1. No polyfilamentous tremolite bundles have been observed, nor any tremolite with an asbestiform habit.

Talc plates have been observed in the mineral mixtures.

The serpentine present in the talc specimens is platy. No chrysotile has been observed in any of the grid preparations. No quartz was observed by AEM.

Mineralogy of the talcs

The mineral content of the seven talc specimens are generally the same, with only the proportions of the minerals varying among the specimens: talc, tremolite, platy serpentine, carbonate mineral, mica(s) and a trace of quartz is present. Only two fibers with properties consistent with a magnesium amphibole have been observed and we would conclude that its content in the talc is trace. Talc fiber is abundant in the specimens, occurring as a finely fibrous material with high aspect ratio. It may be the agalite form of the mineral. The talc fibers are also mineral mixtures, structurally talc and a magnesium

amphibole 5 . These minerals are also mixtures compositionally. The tremolite contained within the talcs occurs as cleavage fragments and is not asbestiform on any level of examination. We have failed to find chrysotile asbestos in these specimens.

⁵ Analyses from Dr. A. Wylies' laboratory in the University of Maryland suggest there may be magnesium amphibole minerals present. This feature may be related more to heterogeneity of specimens than analytical methodology.

COMPARISON OF THE 1976 ROHL TALC REPORT TO NIOSH AND ANALYSES PERFORMED IN 1988

The 1976 report to NIOSH by Dr. Rohl conveys a different sense of the problem as compared to the analyses made recently. We offer the following as explanations for these disparate results.

- 1) Instrumentation: Dr. Rohl did not have an analytical electron microscope available for use in his fiber analysis. He used a transmission electron microscope to obtain morphological and structural information, and then transferred his grids to another, separate, instrument in order to obtain chemical data. This latter instrument, a scanning electron microscope, was interfaced with an energy dispersive x-ray detector. The SEM was operated in the transmitted electron mode which rendered it incapable of resolving fine structures within objects. The finer fibers, especially the fibrous talcs, could not be distinguished from lath-like amphiboles. The nature of the electron optical system was such that talc, anthophyllite, tremolite, talc-anthophyllite. or any talc magnesium amphibole mixture could not be distinguished from each other. This instrumental configuration did not provide the analyst the access to crucial morphological and structural data for fibers which produced chemical data. These shortcomings were significant and we believe severely limited the analysis.
- 2) <u>Mineral Standards</u>: The mineral standards used by Dr. Rohl for "quantitation" of minerals had two shortcomings: first, the standards were <u>binary</u> mixtures of mineral "X" dispersed in a talc matrix. The Vanderbilt specimens are <u>complex mixtures</u>, whose matrix character is

reflections are present. This is especially so for the tremolite which hampers and/or prevents resolution of other amphiboles which may be present, and quartz. Overlapping of diagnostic reflections is a significant shortcoming. Secondly, the matrix of the Vanderbilt specimens is not talc, but rather tremolite. On this basis reflection areas produced by binary mixtures cannot be used for the quantifying of complex mixtures. These shortcomings were known to, and recognized by, Dr. Rohl. He stated in his report: "Because of the large amounts of tremolite (50-60%) present in Sample X, anthophyllite could not be quantitatively determined by x-ray diffraction." We also believe that the tremolite present in the four specimens which assayed positively for anthophyllite interfered with the analysis to such an extent that identification and quantitation of anthophyllite was impossible to make.

3) Interferences with Anthophyllite¹: Rohl used the (210) reflection of anthophyllite (located at about 10.7⁰ two theta) as his diagnostic reflection for quantitation. Tremolite's (110) reflection is located at about 10.6° two theta. The tremolite peak, when intense, may span an entire degree two theta. We consider the difficulties of resolving the anthophyllite peak (at most a shoulder on the tremolite peak) in specimens in which the tremolite is the major mineral phase so great as to render the analysis virtually impossible to make. The standard binary dilution curve of anthophyllite in a talc matrix shows that the 5% assay displays an 8.26Å reflection with an expressed area under the peak of about 1 inch square (by polar planimeter). Although we have been able to detect a small shoulder on tremolite peak in the

¹ The question is whether or not the magnesium amphibole is anthophyllite or another monoclinic variety. Anthophyllite was the mineral identified by Rohl.

specimens examined, we cannot assign it to a specific mineral. The d-spacing of this peak is at about 8.19\AA and this shift in position (the [210] for anthophyllite is at 8.26\AA) coupled with no mineral fiber visible by PLM with indices parallel to length greater than 1.608, suggests that anthophyllite may be present as a trace mineral only. The only other peak which could be used is the 3.03\AA reflection which Drs. Langer and Nolan consider to be a carbonate mineral, (calcite's (104) reflection occurs at 3.03\AA).

- 4) We believe that the <u>quartz analysis</u> was confounded by the presence of tremolite and that the standard dilution of quartz in talc cannot be used with any certainty with the current tremolite matrix.
- 5) We believe that the use of a single d-spacing, $5.3\mathring{\underline{A}}$, cannot be used to characterize amphiboles in a complex silicate matrix. This repeat is non-specific in that diffraction nets displayed by sheet silicates, e.g., <u>talc</u>, also shows this periodicity. This would especially be the case for talc fibers.
- 6) Since 1976 there have appeared in the mineralogical literature reports concerning the complex crystallographical character of amphiboles. Included among these reports are those which refer to mineral structure mixtures, i.e., talcboles, or biopyroboles, in which minerals reflect modified unit cell growth (e.g. b=27Å) rather than those standard cells anticipated for talc (b=9Å) or e.g., anthophyllite (b=18Å). The work of Veblen, Buseck et al, Hutchinson, Crawford, Zussman et al, among many, have shown that some amphiboles originating in metamorphic terrains may display these characteristics (e.g. b=27Å). Talc-magnesium amphibole may represent mineral mixtures, and discrete domains of minerals intermixed on a larger scale (hundreds of unit cells).

7) Since 1976, meetings in New York (NYAS, 330, Health Effects of Asbestos), Washington (NBS-Definitions...etc.), NAS-NRC (Effects of Non-Occupational Exposure..etc.) have underscored the importance of correct terminology in defining asbestos. Mineralogically the tremolite present in the talc specimens meets the criteria for a cleavage fragment. To refer to it as asbestiform is incorrect.